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## INFLUENCE OF THE INTEGRATION LIMITS ON THE SHAPE OF PAIR CORRELATION FUNCTIONS OF NON-CRYSTALLINE MATERIALS

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Influence of the termination effect on the shape of pair correlation functions and values of structural parameters of liquid and amorphous materials has been investigated. It is shown that termination of the diffraction curve at  $Q_{\min} > 0$  rather strongly affects the region around the first peak of  $g(r)$  especially its left flank. On the other hand, presence or absence of a prepeak at low  $Q$ -values of the structure factor does not bring any difference to the pair correlation functions. Decreasing of the upper limit of the diffraction vector causes shift, decrease and broadening of the first peak of the pair correlation function. Besides, this yields spurious oscillations in the vicinity of the first and the second maximum of  $g(r)$  of the liquid and amorphous materials. Therefore straightforward interpretation of the experimental data may be misleading. Some procedures to solve the problem are considered.

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**Keywords:** Liquid and amorphous materials, Structure factors, Pair correlation functions, Termination effect

### 1. Introduction

Studies of non-crystalline structure are mainly based on the experimental determination of the X-ray or neutron diffraction curve as a function of the scattering vector  $Q$  ( $Q = (4\pi/\lambda)\sin\theta$ , where  $\lambda$  is the used wavelength and  $\theta$  is half the scattering angle). Transformation of the scattering intensity  $I=I(Q)$  to the pair correlation function  $g(r)$  and (or) to the radial distribution function  $4\pi r^2\rho(r)$  yields such structural characteristics as the nearest neighbour distance  $r'$  and the coordination number of the first coordination sphere as well as corresponding values for the higher coordination spheres which are important parameters of the short- and medium-range order.

The pair distribution function  $g(r)$  can be calculated by Fourier transformation of the  $S(Q)$  spectrum using the standard transformation technique:

$$g(r) = \frac{\rho(r)}{\rho_0} = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^\infty Q[S(Q) - 1] \sin(Q \cdot r) dQ \quad (1)$$

Here  $\rho(r)$  and  $\rho_0$  are the local and average number densities, respectively, and  $S(Q)$  is the Faber-Ziman total structure factor [1] obtained from the coherent scattering intensity:

$$S(Q) = \frac{I_{e.u.}^{coh}(Q) - \langle f^2(Q) \rangle - \langle f(Q) \rangle^2}{\langle f(Q) \rangle^2} \quad (2)$$

$$\text{with} \quad \langle f^2(Q) \rangle = \sum_j c_j f_j^2(Q), \quad \langle f(Q) \rangle = \sum_j c_j f_j(Q), \quad (3)$$

where  $c_j$  is the mole fraction and  $f_j(Q)$  the total atomic scattering factor of the  $j$ -th component in the alloy.

The position of the first maximum of  $g(r)$  is the mean nearest neighbour distance  $r^I$ . The coordination number

$$N = \int_{r_1}^{r_2} 4\pi r^2 \rho(r) dr \quad (4)$$

is the mean number of atoms within the coordination sphere limited by  $r_1$  and  $r_2$ . The first coordination number can be estimated by several methods. Most commonly used ones are: i) symmetrical (the coordination shell is considered as symmetrical about a first maximum in the  $g(r)$  curve, i.e. the right-hand side of the peak is made symmetrical with that on the left) and ii) integration from the left-hand edge of the first peak to the first minimum in the radial distribution function.

The transform in Eq.(1) requires data from  $Q = 0$  to  $Q = \infty$ . In principle, the scattering intensity can be measured down to  $Q = 0$ . However, experimental limitations and in some cases additional small angle scattering lead to a lower limit  $Q_{\min} > 0$  for each diffraction experiment. On the other hand, the diffraction vector is terminated by a certain value  $Q_{\max}$  which is determined by the wavelength used:  $Q_{\max} = 4\pi/\lambda$ . As a result, the integrand in Eq.(1) is limited by  $Q_{\min}$  and  $Q_{\max}$ , that is:

$$g^{\text{exp}}(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_{Q_{\min}}^{Q_{\max}} Q [S(Q) - 1] \sin(Q \cdot r) dQ \quad (5)$$

Due to such limitation of the diffraction vector, the resulting pair distribution function  $g^{\text{exp}}(r)$  differs from the ideal  $g(r)$ . So-called termination or truncation effect yields spurious details on the pair correlation functions. This deforms the radial distribution functions, changes the position and profile of the maxima and minima and introduces errors in the calculated coordination numbers [2–5].

In this paper we examine influence of the termination effect on the shape of the pair correlation functions of the non-crystalline materials with low-coordinated (open) structure. Liquid Te and amorphous Ge-telluride have been chosen for the investigation.

## 2. Experimental

Neutron scattering experiment on liquid Te has been carried out on the double-axis spectrometer of the research reactor at Rossendorf. The neutron wavelength was  $\lambda = 0.91 \text{ \AA}$  and the accessible  $Q$ -values range – from  $1.0 \text{ \AA}^{-1}$  to  $9.35 \text{ \AA}^{-1}$ . The sample was contained in a sealed quartz tube (internal diameter 15 mm, wall thickness 1 mm). The overall uncertainty in the sample temperature was smaller than 5 K. The data correction procedure has been described in [6].

The X-ray diffraction experiments were performed with a  $\theta$ - $\theta$  diffractometer using  $\text{MoK}\alpha$ -radiation which has been selected by a focusing graphite monochromator placed in the diffracted beam. The X-ray intensity scattered at the free surface was measured by a scintillation detector with a pulse height analyser. The liquid Te temperature was constant within an error of about 1 K. The scattering intensity has been measured from  $1.0$  to  $11.85 \text{ \AA}^{-1}$  of  $Q$  in the case of liquid Te.

The amorphous  $\text{Ge}_{25}\text{Te}_{75}$  alloy was prepared by the melt-spinning technique. The X-ray intensity diffracted by the amorphous sample at room temperature was counted over the range of  $Q$  between  $0.5$  and  $12.5 \text{ \AA}^{-1}$ . The correction and normalization of the experimental data were done as described in [7–9].

### 3. Results and discussion

#### 3.1. Liquid Tellurium

The experimental structure factors of liquid Te at 550 °C (neutron diffraction) and 500 °C (X-ray diffraction) are shown in Fig. 1. The differences between the results of X-ray and neutron scattering are mainly caused by the rather sensitive absorption correction of the neutron experiment. In both cases scattered intensity has been measured down to  $Q_{\min} = 1.0 \text{ \AA}^{-1}$ . For smaller  $Q$ -values we have employed a parabolic extrapolation of  $S(Q)$ :

$$S(Q) = S(0) + AQ^2. \quad (6)$$

The value of  $S(0) = 0.062$  has been taken from Ref. [10] and the coefficient  $A$  was determined by fitting the extrapolation function to the experimental  $S(Q)$  at  $Q = Q_{\min}$ .

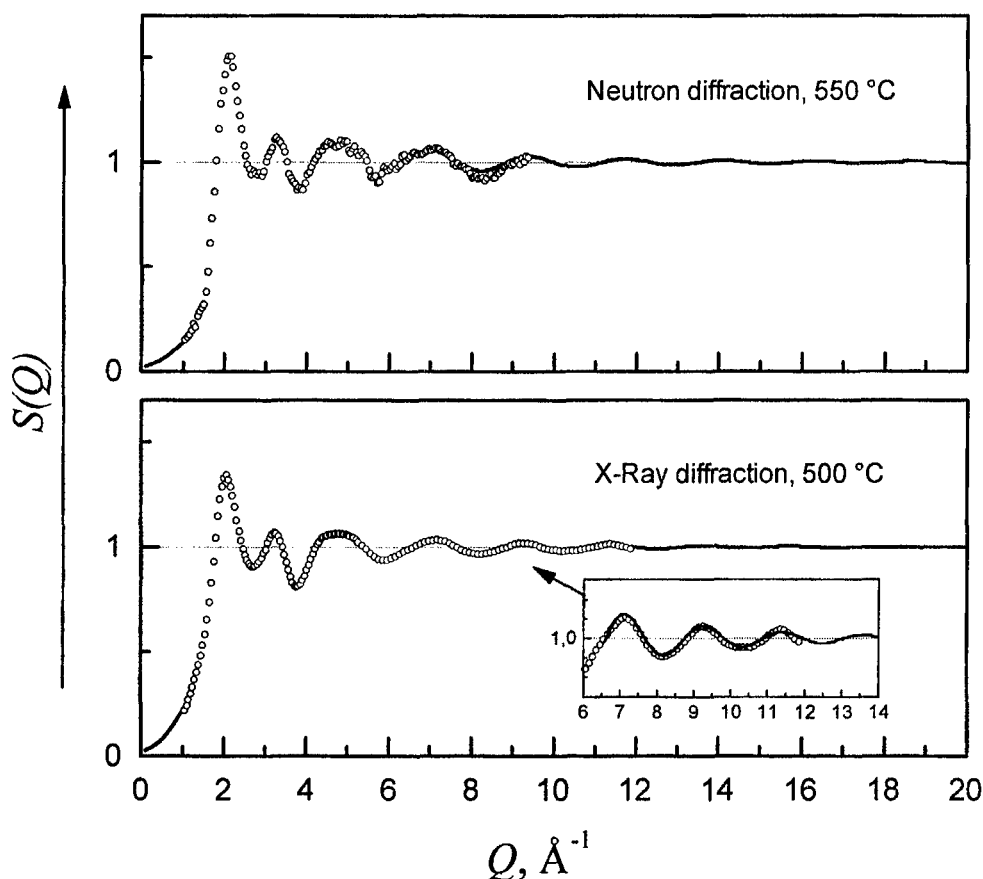
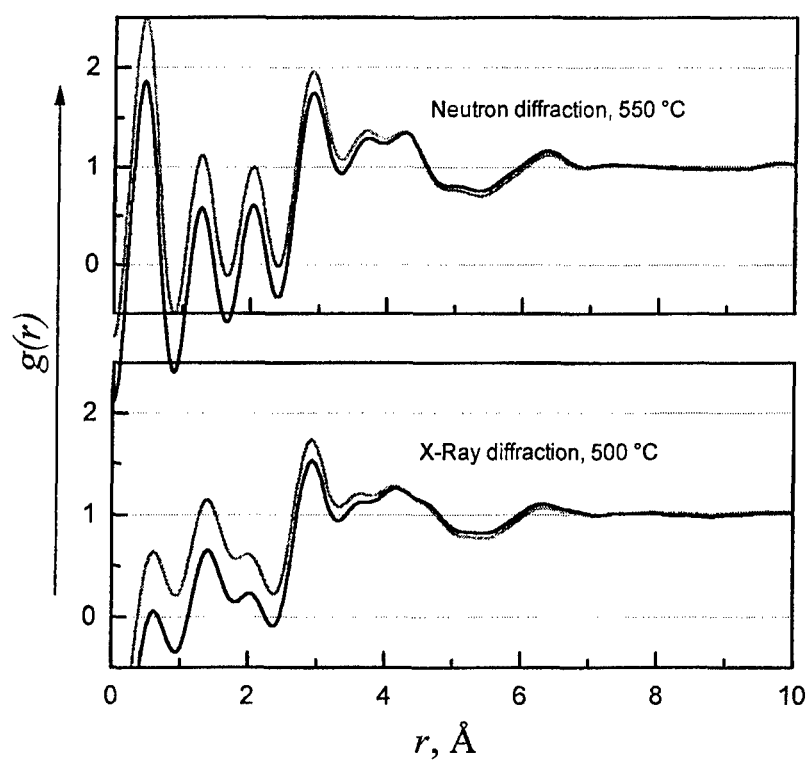
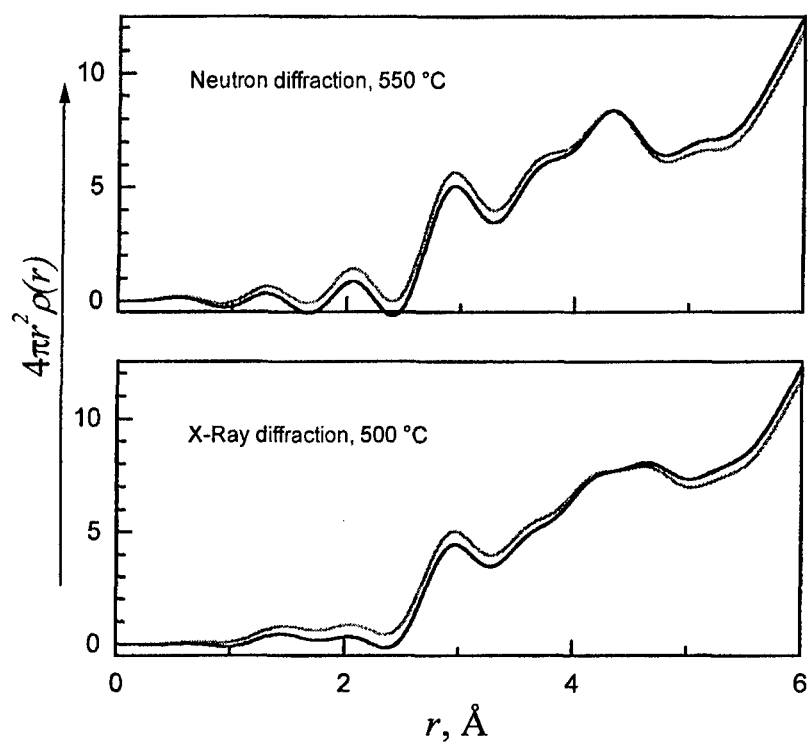


Fig. 1. Structure factors of the liquid Te: *circles* – experimental results; *lines* – extrapolation.

Fig. 2 shows the pair correlation and radial distribution functions calculated with Eq. (5) using lower integration limits of  $Q_{\min} = 0 \text{ \AA}^{-1}$  and  $Q_{\min} = 1.0 \text{ \AA}^{-1}$ . The upper integration limit was  $Q_{\max} = 9.35 \text{ \AA}^{-1}$  for neutrons and  $Q_{\max} = 11.85 \text{ \AA}^{-1}$  for X-rays. It is very good seen that the region around the first coordination shell, especially its left flank, is rather strongly affected. Termination of the structure factor at  $Q_{\min} > 0$  substantially increases the pair correlation and radial distribution function in the region of the first maximum that yields overestimated coordination number.



a)



b)

Fig. 2. Pair correlation (a) and radial distribution (b) functions of liquid Te calculated with different integration limits  $Q_{\min}$ : black lines -  $Q_{\min} = 0 \text{ Å}^{-1}$ ; gray lines -  $Q_{\min} = 1.0 \text{ Å}^{-1}$ .

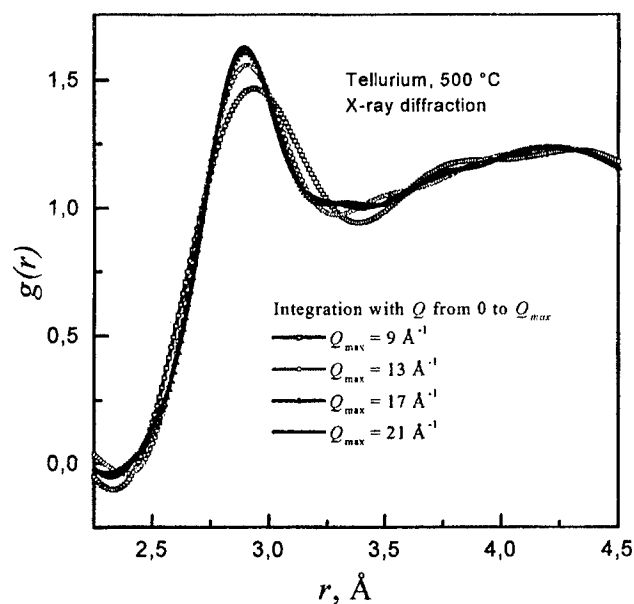


Fig. 3. Pair correlation function of liquid Te calculated with different integration limits  $Q_{\max}$ .

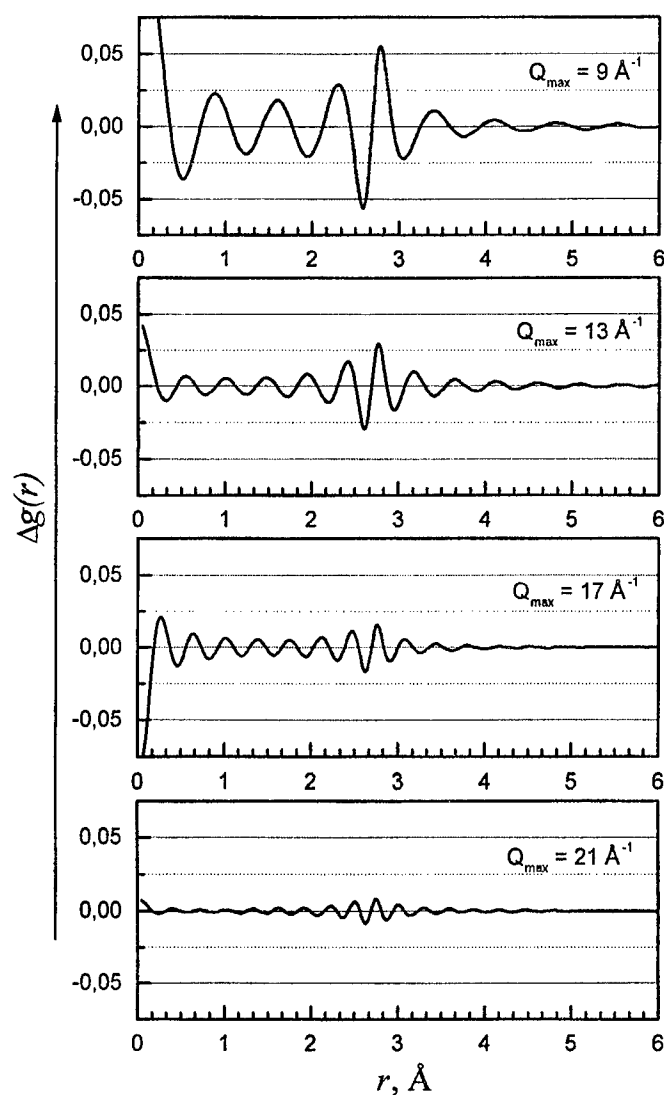


Fig. 4. Residual pair correlation function  $\Delta g(r)$  calculated with  $S(Q)$  from  $Q_{\max}$  to  $\infty$ .

The next step was to examine the effect of the structure factor termination at high  $Q$ -values. For this purpose we have extrapolated the experimental structure factor for  $Q > Q_{\max}$  using the function

$$S(Q) = 1 + c_1 \cos(c_2 Q - c_3) \exp(-c_4 Q) / Q \quad (7)$$

which enables one to obtain an analytical expression for  $g(r)$  up to infinity. The parameters  $c_1 \dots c_4$  have been determined by a least squares fit of the high  $Q$ -region of the experimental  $S(Q)$ . The extrapolated parts of the liquid Te structure factors are given in Fig. 1.

In Fig. 3 the region of the first and the second maximum of the pair correlation function of liquid Te at 500 °C calculated with different upper  $Q$ -limit is shown. It is seen that with increasing  $Q_{\max}$  the height of the first peak increases while its width decreases. Besides, the position of the first maximum is shifted to the smaller  $r$ -values and "false" oscillations disappear.

Fig. 4 illustrates the termination error in  $g(r)$  by limiting the structure factor to  $Q_{\max} = 9, 13, 17$  and  $21 \text{ \AA}^{-1}$ . It is seen that the high-angle contribution to the pair correlation function

$$\Delta g(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_{Q_{\max}}^{\infty} Q [S(Q) - 1] \sin(Q \cdot r) dQ \quad (8)$$

is the most essential in the vicinity of the first and the second peak.

The pair correlation functions of the liquid Te calculated with different lower and upper integration limits in Eq. (5) are presented in Fig. 5. It is seen that both limitations significantly affect the resulting curve, especially in the range of the first and the second coordination spheres. Therefore a straightforward interpretation of the "experimental" pair correlation functions may be misleading.

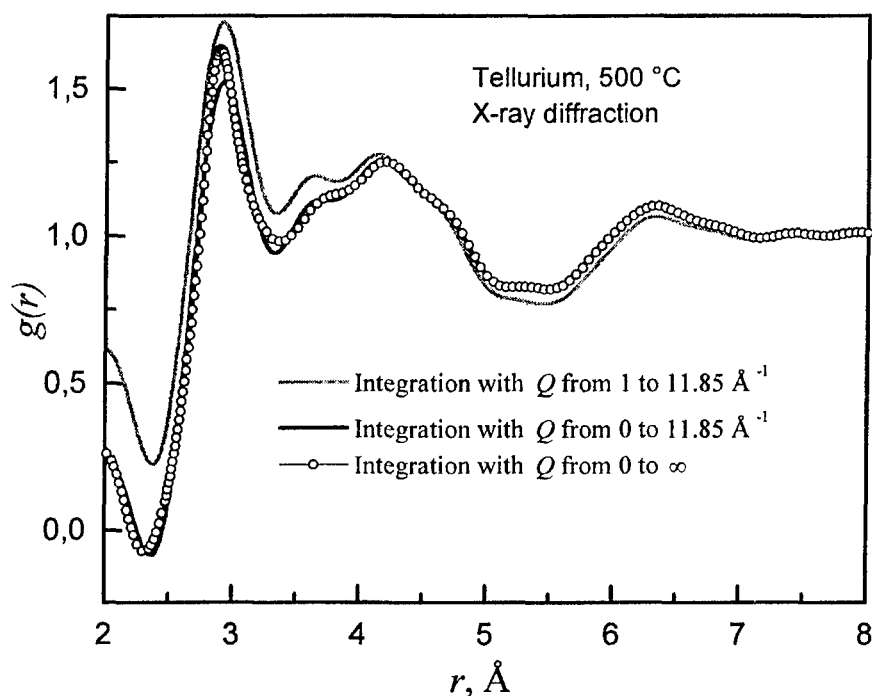


Fig. 5. Pair correlation functions of the liquid Te calculated with different integration limits  $Q_{\min}$  and  $Q_{\max}$ .

In Fig. 6 we show some structural parameters of liquid Te in dependence on the upper integration limit  $Q_{\max}$ . The nearest neighbour distance  $r^j$  and coordination number  $N^j$  continuously decrease with increasing  $Q_{\max}$  up to  $19 - 20 \text{ \AA}^{-1}$  while the value of  $g(r^j)$  increases. Beginning with

$Q_{\max} \sim 20 \text{ \AA}^{-1}$  all parameters remain practically unchanged. This is in good correspondence with the result shown in Fig. 4. Indeed, the residual pair correlation function  $\Delta g(r)$  becomes very small when  $Q_{\max}$  achieves  $\sim 21 \text{ \AA}^{-1}$  or more.

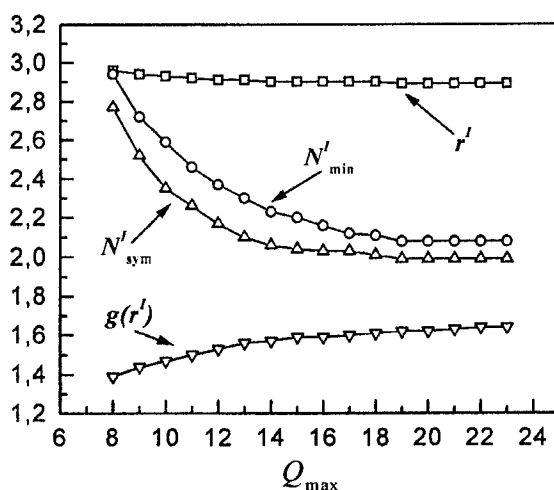


Fig. 6. Nearest neighbour distance  $r^I$ , coordination number  $N^I_{\min}$ ,  $N^I_{\text{sym}}$  and  $g(r^I)$  as a function of  $Q_{\max}$  ( $Q_{\min} = 0$ ).

### 3.2. Amorphous $\text{Ge}_{25}\text{Te}_{75}$

The experimental structure factor of the amorphous  $\text{Ge}_{25}\text{Te}_{75}$  alloy measured at room temperature is shown in Fig. 7. It is seen that the modulations of the  $S(Q)$  of the amorphous Telluride are much more pronounced than those of liquid objects (e. g. liquid Te). Besides the shape of the maxima and minima in the  $S(Q)$  of the  $\alpha\text{-Ge}_{25}\text{Te}_{75}$  alloy are much more complex than that in the hard-sphere structure factor. This means that one can not analytically extrapolate the experimental structure factor in the same or similar manner as we did it for the liquid Te. In such cases it is better to use experimental data up to the limited value of the diffraction vector  $Q_{\max}$  than to introduce additional errors employing a theoretical function for  $Q > Q_{\max}$ .

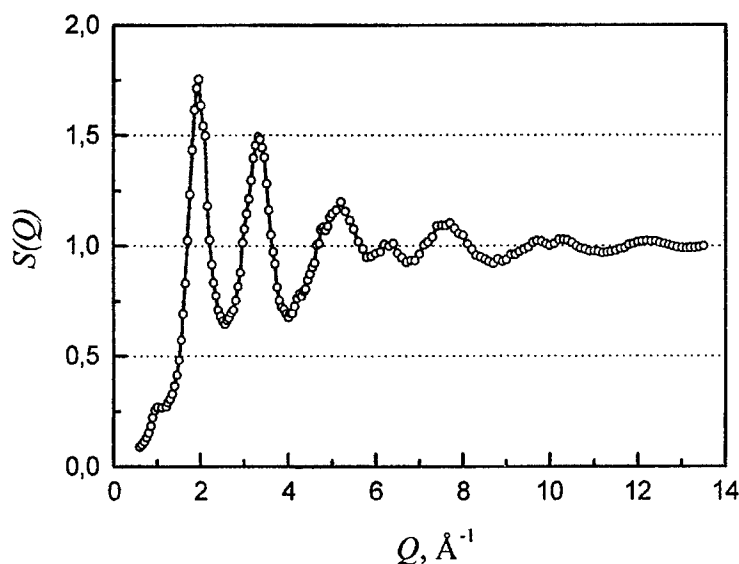


Fig. 7. Experimental structure factor of the amorphous  $\text{Ge}_{25}\text{Te}_{75}$  alloy.

As we have seen above, the termination of the structure factor at  $Q = Q_{\max}$  yields ghost oscillations in the vicinity of the first peak of the pair correlation function. It is very interesting and



important to know whether these false modulations depend on the value of  $Q_{\max}$  with regard to the shape of the structure factor. In order to test it, we have calculated the residual pair correlation function using Eq. (8) with different limit  $Q_{\max}$ . As a structure factor we employed the analytical function given by Eq. (7) with parameters  $c_1 = 0.9239$ ,  $c_2 = 2.8576$ ,  $c_3 = 20.2316$ ,  $c_4 = 0.2012$ . Figs. 8 and 9 show the high-angle contribution to the pair correlation function  $\Delta g(r)$  in dependence on  $Q_{\max}$ . The oscillations of the residual pair correlation function are the greatest when the structure factor is terminated at the position where the  $S(Q)$  equals unity and shows maximum slope (e.g. at  $13.1 \text{ \AA}^{-1}$  and  $14.2 \text{ \AA}^{-1}$ ). On the other hand, oscillations of the  $\Delta g(r)$  are minimal when  $Q_{\max}$  falls at the position of a minimum or a maximum (e.g. at  $13.7 \text{ \AA}^{-1}$ ) at the end of the structure factor where the slope of  $S(Q)$  is zero.

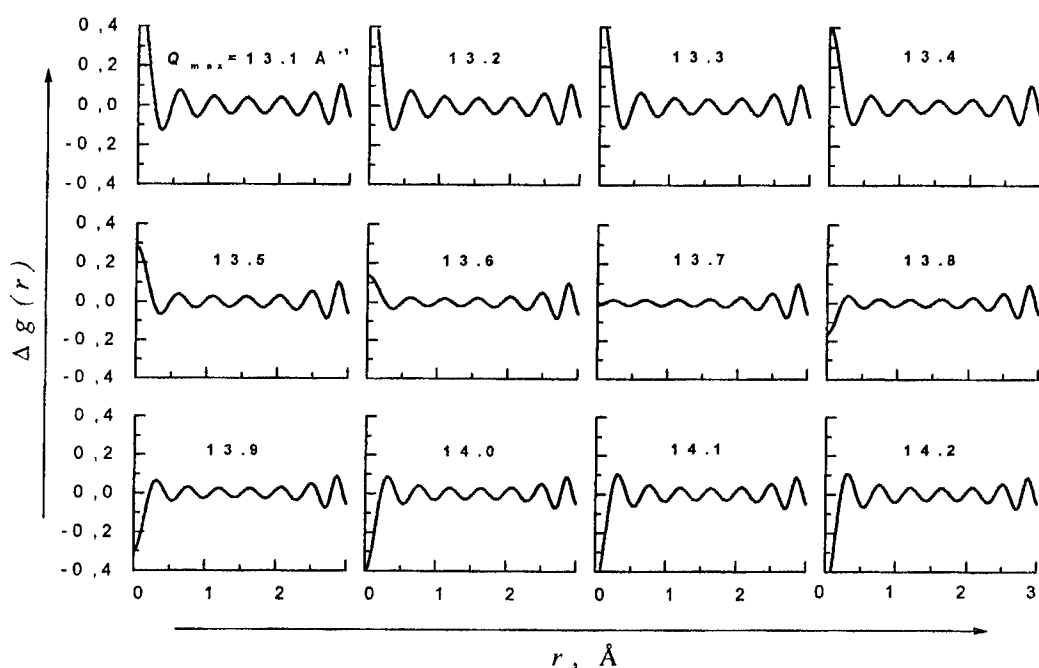


Fig. 8. Residual pair correlation function  $\Delta g(r)$  calculated with  $S(Q)$  from  $Q_{\max}$  to  $\infty$ .

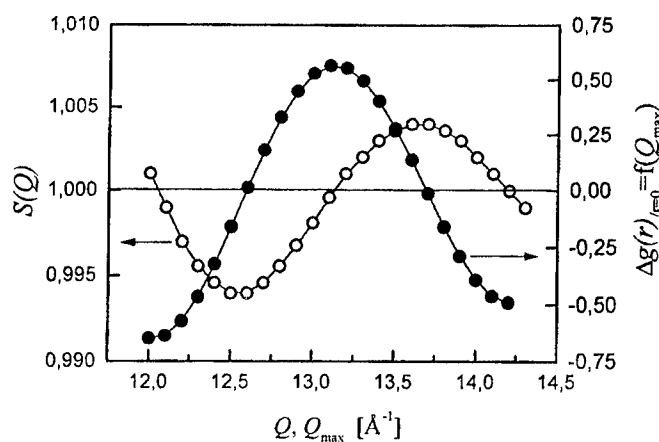


Fig. 9.  $\Delta g(r)|_{r=0}$  as a function of  $Q_{\max}$  in Eq.(8).  $S(Q)$  – part of the structure factor of liquid Te at  $500^\circ \text{C}$  (as in Fig. 1).

Taking into account the result mentioned above we have truncated the experimental structure factor of the  $\alpha\text{-Ge}_{25}\text{Te}_{75}$  alloy at  $Q_{\max}$  of  $11.2$  and  $13.5 \text{ \AA}^{-1}$  that respects to the position of the minimum at the end of curve. Fig. 10 illustrates that decrease of the upper integration limit in Eq. (5) causes

decrease, shift and broadening of the first peak and yields spurious oscillations in the pair correlation functions of the amorphous material in the same manner as in the case of liquids.

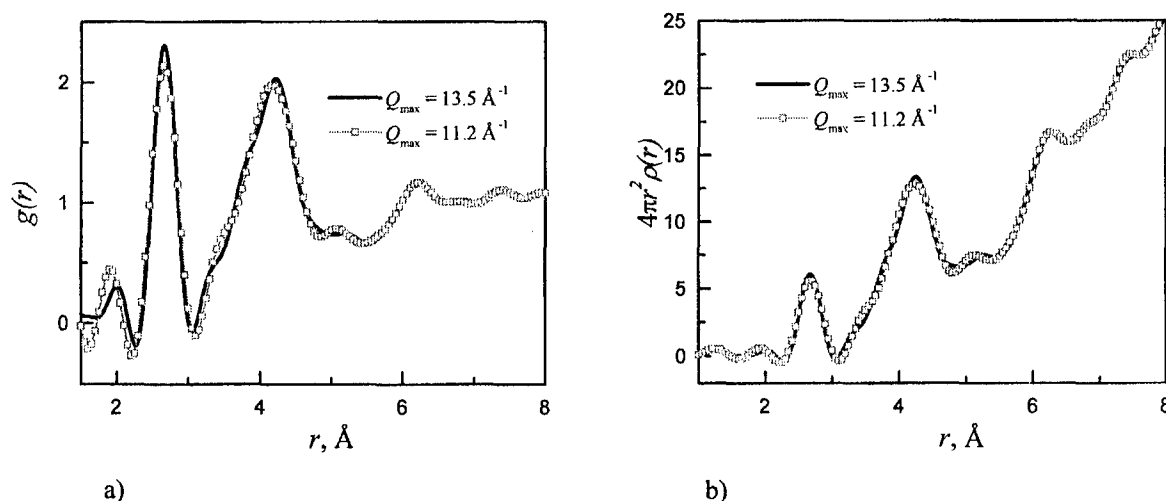


Fig. 10. Pair correlation (a) and radial distribution (b) functions of amorphous  $\text{Ge}_{25}\text{Te}_{75}$  alloy calculated with different integration limits  $Q_{\max}$ .

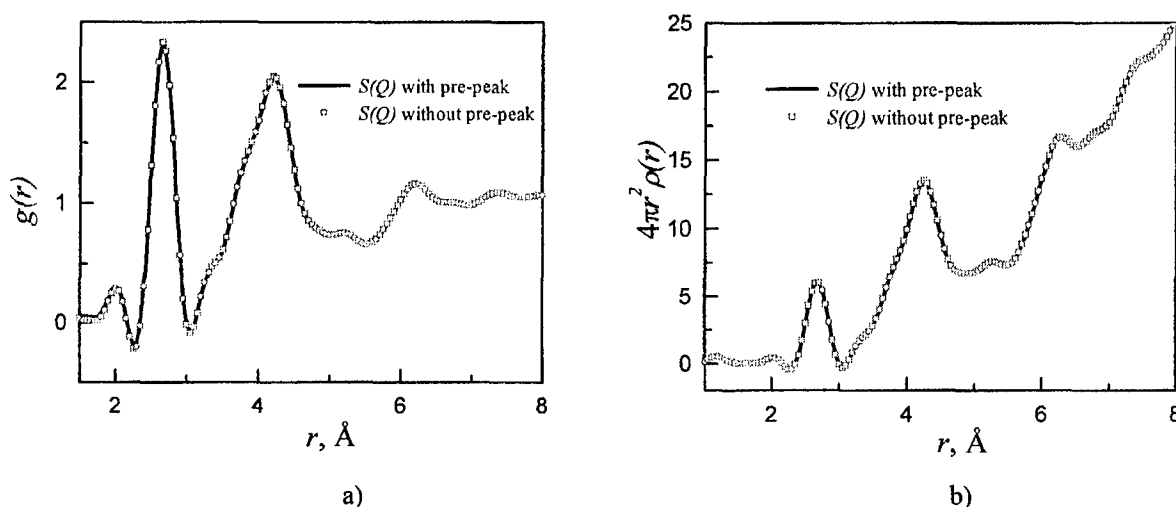


Fig. 11. Pair correlation (a) and radial distribution (b) functions of amorphous  $\text{Ge}_{25}\text{Te}_{75}$  alloy.

In the experimental structure factor of the  $\alpha\text{-Ge}_{25}\text{Te}_{75}$  alloy (Fig. 7) one can see a small prepeak at  $Q = 1.1 \text{ \AA}^{-1}$ . It is generally assumed that i) this feature of the diffraction pattern is associated with medium-range order (MRO) and (or) ii) prepeak reflects strong bonding of unlike atoms. As regards the amorphous  $\text{Ge}_{25}\text{Te}_{75}$  alloy we believe that the prepeak in the structure factor arises due to connection of Ge and Te atoms. However in the present paper we would like to examine whether and how the shape of the pair correlation function depends on the prepeak. Therefore we calculated pair correlation function using experimental structure factor i) from  $Q_{\min} = 0.5 \text{ \AA}^{-1}$  to  $Q_{\max} = 13.5 \text{ \AA}^{-1}$ ; and ii) from  $Q_{\min} = 1.5 \text{ \AA}^{-1}$  to  $Q_{\max} = 13.5 \text{ \AA}^{-1}$ . In both cases  $S(Q)$  was extrapolated from  $S(Q_{\min})$  to  $S(0)$  as described above for the liquid Te. As one can see from Fig. 11 there is practically no difference between pair correlation functions calculated with structure factor containing prepeak and without that.

#### 4. Conclusions

Limitation of the experimental scattering intensity at certain values of the diffraction vector  $Q_{\min}$  and  $Q_{\max}$  that differ from zero and infinity, respectively, yields spurious details on the pair correlation functions and introduces errors in the calculated structural parameters of the liquid and amorphous materials.

Termination of the diffraction curve at  $Q_{\min} > 0$  significantly increases the pair correlation and radial distribution functions in the region of the first maximum that yields overestimated coordination number.

Termination of the structure factor at high  $Q$ -values of the diffraction vector causes shift, decreasing and broadening of the first peak of the pair correlation functions. In addition, this results in spurious oscillations in the vicinity of the first and the second maximum of  $g(r)$ .

Termination effect in the pair correlation functions can be eliminated or significantly reduced by extrapolation of the experimental scattering intensity or structure factor to zero and to infinity using analytical functions. In cases when this cannot be done the termination at high  $Q$ -values should be made at the position of minimum or maximum of the structure factor.

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